Exploiting supramolecular chemistry in metal recovery: novel zwitterionic extractants for nickel(II) salts†

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Hexadentate tris-salicylaldimine ligands bearing *ortho-N*-dialkylaminomethyl substituents have been shown to function as ditopic ligands for $NiSO_4$ or $NiCl_2$. The incorporation of the Ni-ion into the $N_3O_3^{3-}$ site templates the pendant alkylammonium groups to allow them to hydrogen bond to the attendant anion(s). Formulation as complexes of the trianionic/tricationic ligand is supported by X-ray structure determinations of solvated forms of the complexes [Ni(L)SO_4] and [Ni(L)Cl]Cl, where L = tris-1,1,1-{2-hydroxy-3-(piperidin-1-ylmethyl)-5-*tert*-butyl-benzaldiminomethyl}ethane. The kerosene-soluble ligand, tris-2,2′,2″-{2-hydroxy-3-(di-n-hexylaminomethyl)-5-nonylbenzaldiminomethyl}amine, functions as a good extractant for nickel salts, showing high selectivity for recovery of $NiCl_2$ over $NiSO_4$. This reagent can be stripped and recycled directly using aqueous ammonia or by first displacing the Ni^{2+} with acid and then neutralising the pendant alkylammonium groups. The acid-stripping is accompanied by hydrolytic degradation of the reagent, but in many other respects this novel class of reagent shows promise in opening up novel flowsheets for nickel recovery, based on transport of the metal salt as opposed to ion-exchange based processes.

Introduction

The processes used in extractive metallurgy have evolved over several thousand years[1] and are based on the unit operations: *concentration, separation, reduction*, and, when high purity metal is required, *refining*.[2-4] The concentration and separation of base metals such as Cu, Ni and Zn present remarkable technical challenges. Typically the production of 1 tonne of electrical grade copper requires the processing of 800 tonne of rock (Fig. 1).
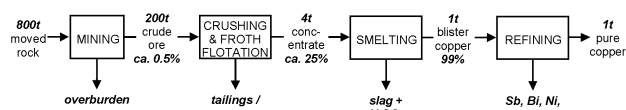

Fig. 1 Flowsheet for recovery of copper from sulfidic ores.[1]

The last four decades have seen a move from *pyro*- towards *hydro*-metallurgical processes for the recovery of such metals, providing an opportunity for the development of selective metal complexing agents to effect the concentration and separation operations. In general, the design criteria for such metal extractants are defined by the "front end" (leaching) and "back end" (reduction) processes in the simplified flowsheet shown in Fig. 2.

Fig. 2 Basic flowsheet for hydrometallurical recovery of base metals.

Ion-exchange reagents and metal ion transport

A range of separation technologies can be used to effect transfer of the desired metal from the aqueous pregnant leach solution (pls). The most commonly used are based on equilibria involving liquid–liquid (solvent extraction) and liquid–solid (ion-exchange and chelating resins) systems. Solvent extraction has the advantage of being easily engineered for continuous operation and has proved remarkably robust since its introduction for uranium production.[5] For recovery of base metals the preferred water-immiscible phase is a high boiling hydrocarbon on grounds of both cost and safety. The use of such non-polar solvents facilitates assembly reactions based on hydrogen-bonding and on ion-pair and ion–dipole interactions of solutes. The exploitation of such supramolecular chemistry is a central theme of this paper, providing the basis for organisation of metal- and anion-binding sites in relatively simple ligands. An essential criterion for any commercial exploitation of organic complexing agents in base metal recovery is that they are inexpensive. A large extractant inventory makes a substantial contribution to capital costs and even when such reagents are recycled in the flowsheet there are always some losses through chemical degradation or entrainment of droplets in the aqueous phases.

One of the most successful base-metal recovery processes involving solvent extraction is illustrated in the flowsheet in Fig. 3. This circuit accounts for more than 25% of worldwide
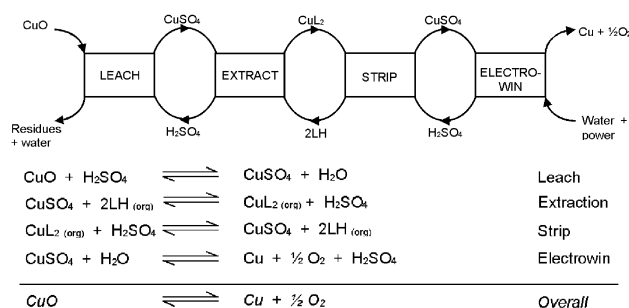

Fig. 3 A simplified flowsheet and materials balance for the recovery of copper from oxidic and transition ores by heap leaching, solvent extraction and electrowinning.

copper production.[6] Its commercial success is based on the very good materials balance which is obtained when processing oxidic ores, using the phenolic oxime "pH-swing" extractants in conjunction with a conventional electrolysis process.[6–8] Acid released on extraction is re-used in leaching and the acid needed for stripping and recycling the extractant is generated by the electrolysis process (see eqns. in Fig. 3).

The relatively "strong" commercial phenolic oxime reagents **1** allow high recovery from pls's which can have pH values as low as 1.5[6] and effect the key separation of Cu from Fe which is often present in comparable or higher concentrations.

**1**   **2**
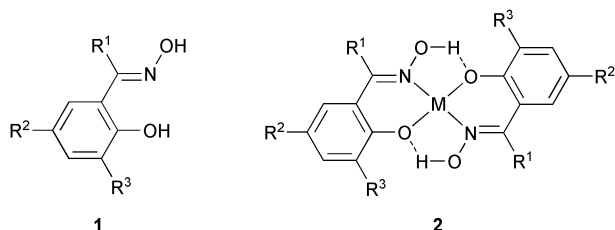
The "strength" of a formulated reagent can be tuned to meet the requirements of a particular feed solution. It can be reduced by selecting ketoximes (**1**, R^1 = Me or Ph) which are generally weaker than the aldoximes, or by the addition of "modifiers" which are materials that hydrogen-bond to the extractants in the hydrocarbon diluents. The competitive formation of lig-and–ligand, ligand–modifier and modifier–complex assemblies in the organic phase influences the efficiency of extraction and provides a very practical application of supramolecular chemistry.[9–14]

In the solid state H-bonding between the oximic OH and phenolate oxygen atoms *within* a complex unit is almost invariably observed in 2 : 1 complexes, leading to pseudo-macrocyclic structures **2** with $N_2O_2^{2-}$ donor sets.[15] A pseudo-macrocyclic structure **3** is also present in the solid state forms of some free ligands[15] and is retained in solution.[16,17] As a consequence they are partially preorganised for complex formation and the dimers should be considered in modelling extraction equilibria.[16,18]

$$[(LH)_2]_{(org)} + M^{2+} \rightleftharpoons [ML_2]_{(org)} + 2H^+ \qquad (1)$$

3
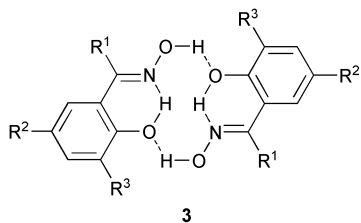
Also, interactions of the monomeric, dimeric or other forms of the extractant with modifiers are important in interpreting extraction equilibria,[16,18] *e.g.* as in

$$LH_{(org)} + Y \rightleftharpoons [LHY]_{(org)} \qquad (2)$$
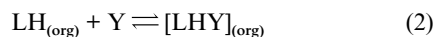
where the modifier competes with metal cations for the donor functionalities. Work in this area has been reviewed[7,16] and the importance of the preorganised dimer in recovery of copper has been established, particularly in saturated hydrocarbon solutions.[18]

It is timely and challenging to investigate the roles of secondary bonding in metal extraction. Assembly processes are essential to modification of reagent strength and probably account for many of the observations of synergistic extraction shown by combinations of reagents. Most importantly for base metal recovery, they provide the possibility of using relatively simple cheap reagents to obtain organised donor sets with high selectivity and strength of extraction.

Reagents transporting metal salts

Whilst pH-swing extractants such as **1** and D2EHPA (di-2-ethylhexylphosphate) find extensive use in hydrometallurgy[9, 19–24] they have limitations when treating certain pls's. When leaching does not consume acid equivalent to metal transferred to the aqueous phase, as is the case in many new oxidative high pressure processes[25,26] to treat sulfidic ores, neutralisation of the raffinate will be required, leading to poor materials balances. Also, the pH-swing extractants are inefficient when treating feeds with high metal contents because the acid released on extraction displaces the equilibrium and only limited metal transfer can be obtained without inter-stage neutralisation. A solution to this problem is provided by using a different mechanism for metal extraction from the aqueous phase, avoiding an exchange process and transporting metal *salts*. This has been proposed for the recovery of base metals by oxidative chloride-leaching of sulfidic ores.[27,28] For the recovery of copper from chalcocite and related ores by ferric chloride leaching this is illustrated in the flowsheet in Fig. 4.
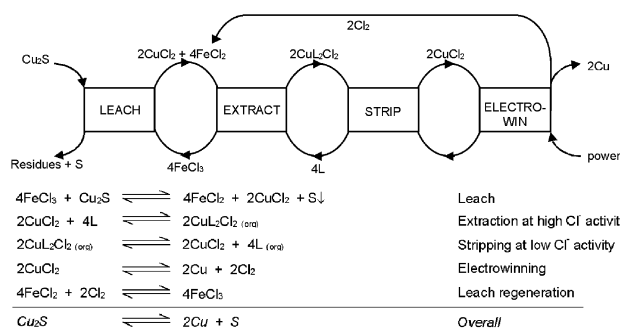

Fig. 4 A simplified flowsheet and materials balance for the recovery of copper from sulfidic ores by chloride leaching, solvent extraction and electrowinning, using for example reagents such as **4**.

Neutral, 'solvating' ligands ‡ such as **4** and **5** have been used in trials for copper[29–31] and zinc[32–34] recovery from chloride media.

CLX50

4   **5**
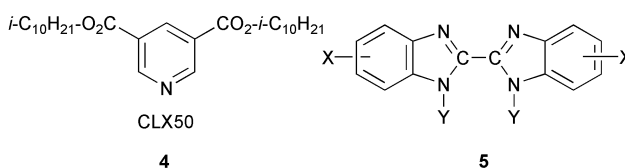
The low activity of water in these feed solutions which have high chloride content results in high proton activity. In addition to the problems this creates with corrosion of plant, there is a tendency for even very weakly basic ligands to become protonated, allowing extraction of Fe(III) by an ion-pairing mechanism,§

$$L_{(org)} + H^+ + FeCl_4^- \rightleftharpoons [LH][FeCl_4]_{(org)} \qquad (3)$$

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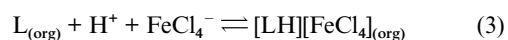
‡ Extraction with neutral or 'solvating' ligands typically involves formation of neutral organic-soluble complexes containing coordinated anions, and the processes use anion concentration to control equilibria, *e.g.*,

$$UO_2^{2+} + 2NO_3^- + 2TBP \rightleftharpoons [UO_2(NO_3)_2TBP_2]$$

where tri-n-butylphosphate (TBP) is used as the solvent and also is involved in the second coordination sphere.
§ Outersphere complex formation, often involving hydrogen bonding, is important in ion-pairing extractants *e.g.* Alamine 36 is an effective extractant for Fe(III) in acidic chloride media:

$$Fe^{3+} + 4Cl^- + H^+ + R_3N_{(org)} \rightleftharpoons FeCl_3\text{–}Cl^- \cdots H\text{–}NR_3^+_{(org)}$$
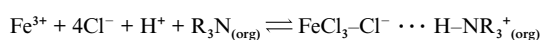
which reduces the otherwise very high Cu/Fe or Zn/Fe selectivity of **4** or **5**. These problems¶ and the engineering costs associated with handling chlorine from the electrolysis of metal chlorides have contributed to the limited commercial exploitation of the chloride-stream technology. Most of these problems would be overcome if a sulfate process stream were used and extractants were available to transport metal *sulfates*. As SO_4^{2-} and HSO_4^- are relatively poor ligands for base metal cations it will be difficult to exploit a transport mechanism based on formation of inner-sphere complexes as used in the chloride flowsheet, Fig. 4. Consequently we have recently developed ditopic ligands with separated metal cation and SO_4^{2-} binding sites.[35,36] The prototypes were based upon tetradentate H_2salen-type molecules bearing tertiary amine groups which on protonation provide the SO_4^{2-} binding sites (Scheme 1).

Proof-of-concept studies[37–39] have established that: (i) incorporation of Ni(II) or Cu(II) into the salen $N_2O_2^{2-}$ site templates the pendant dialkylammonium groups to facilitate binding of SO_4^{2-}, (ii) the binding of the metal sulfate into a *zwitterionic* form of the ligand provides a convenient pH-swing based protocol for sequential stripping of the cation and anion, recycling the ligand and generating a concentrated metal sulfate solution for electrowinning, and (iii) hydrophobic forms of the ligands are easily prepared from commercial 2-hydroxy-5-alkylbenzaldehydes. This paper deals with the development of systems which could be used to recover nickel from oxidative leaching of sulfidic ores based on a flowsheet as outlined in Fig. 5.
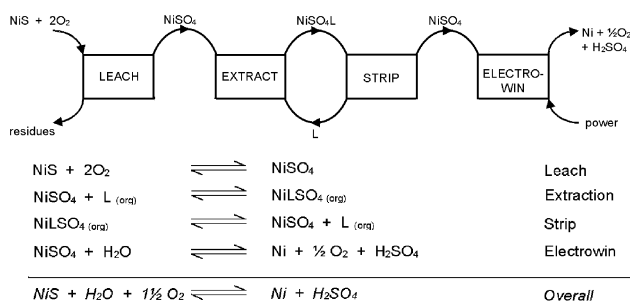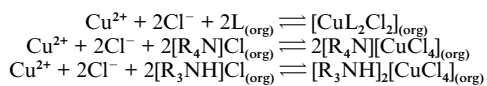
Fig. 5 A flowsheet and materials balance for recovery of metals from sulfidic ores using oxidative leaching, solvent extraction of metal sulfate and electrowinning.
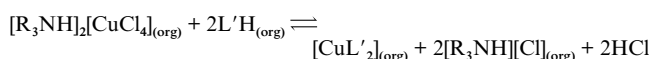
¶ Phenolic-oxime reagents such as **1** have also been used[63] to recover copper from chloride leach solutions,

$$2L'H_{(org)} + CuCl_2 \rightleftharpoons CuL'_{2(org)} + 2HCl$$
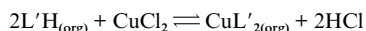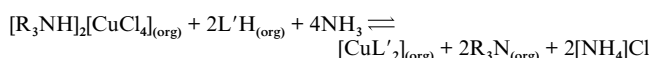
but the high proton activity in these feeds limits the efficiency of these processes and steps have to be taken to adjust and control pH.[29,64] A creative solution to this problem based on using a mixture of a "pH-swing" extractant L'H and either a solvating or an ion-pairing extractant has been reviewed recently.[64,65] On contacting the aqueous feed the majority of the copper extracted is transferred to the organic phase by the solvating or ion-pairing reagents, *e.g.*

$$Cu^{2+} + 2Cl^- + 2L_{(org)} \rightleftharpoons [CuL_2Cl_2]_{(org)}$$
$$Cu^{2+} + 2Cl^- + 2[R_4N]Cl_{(org)} \rightleftharpoons 2[R_4N][CuCl_4]_{(org)}$$
$$Cu^{2+} + 2Cl^- + 2[R_3NH]Cl_{(org)} \rightleftharpoons [R_3NH]_2[CuCl_4]_{(org)}$$

Scrubbing the loaded organic phase with water or ammonia removes HCl, transferring the copper to the "pH-swing" extractant as in

$$[R_3NH]_2[CuCl_4]_{(org)} + 2L'H_{(org)} \rightleftharpoons$$
$$[CuL'_2]_{(org)} + 2[R_3NH][Cl]_{(org)} + 2HCl$$

or

$$[R_3NH]_2[CuCl_4]_{(org)} + 2L'H_{(org)} + 4NH_3 \rightleftharpoons$$
$$[CuL'_2]_{(org)} + 2R_3N_{(org)} + 2[NH_4]Cl$$

which then can be stripped with sulfuric acid to give a sulfate electrolyte for conventional electrowinning.[64–70]
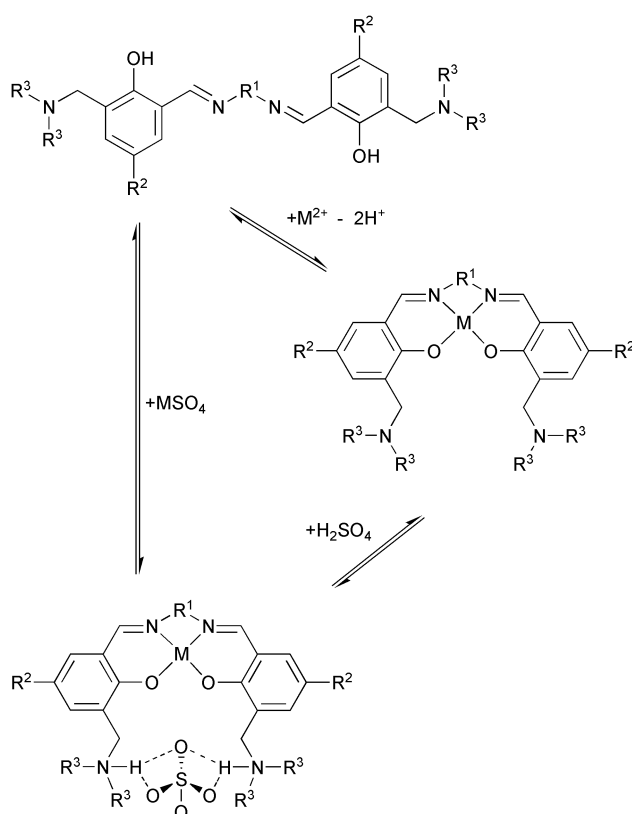
Scheme 1 Formation of metal sulfate and "metal only" complexes from ditopic salenH$_2$ ligands with pendant dialkylaminomethyl groups.

Experimental

Instrumentation

Fast atom bombardment (FAB) mass spectra were obtained on a Kratos MS50TC spectrometer in thioglycerol (thio) or 3-nitrobenzyl alchol (3-noba) matrices and electrospray mass spectra on a Finnigan Mat LCQ spectrometer. Inductively coupled plasma atomic emission spectroscopy (ICP-OES) analysis for Ni and S was performed on Thermo Jarrel Ash IRIS ICP-OES equipment.[37,38] C, H, N contents were obtained on a Perkin-Elmer 2400 elemental analyser by the University of Edinburgh Microanalytical Service.

Solvent and reagent pre-treatment

All reagents and solvents were used as received with the exception of triethylenetetramine which was distilled before use. Orform SX7 was obtained from Avecia.

Ligand synthesis

The 2-hydroxy-5-alkylbenzaldehydes and ethoxy-*N*-piperidinylmethane were prepared by the methods described previously by Levin[40] and Fenton and co-workers.[41] *cis,cis*-1,3,5-Triaminocyclohexane (tach) was synthesised according to the method of Bowen and co-workers.[42]

Compound 6. 2-Hydroxy-3-(morpholin-4-ylmethyl)-5-methylbenzaldehyde (3.4 g, 14.3 mmol) in diethyl ether (30 ml) was added to a solution of triethylenetetramine (tren) (0.7 g, 4.8 mmol) in ethanol (30 ml). The resultant yellow solution was stirred at room temperature for 72 h then concentrated *in vacuo* to give a yellow oil which on tritutation in pentane/diisopropyl ether at −78 °C gave a yellow solid which was collected by filtration and dried *in vacuo* (2.7 g, 71%); MS (electrospray) *m/z*, 798 (MH$^+$ 100%). Crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a dichloromethane solution.

Compound 7. 2-Hydroxy-3-(piperidin-1-ylmethyl)-5-*tert*-butylbenzaldehyde (2.3 g, 8.3 mmol) in diethyl ether (30 ml) was added to a solution of triethylenetetramine (tren) (0.4 g, 2.7 mmol) in ethanol (25 ml). The resultant orange solution was stirred at room temperature overnight then concentrated *in vacuo* to give an orange oil. The yellow oil was recrystallised from hexane to give a yellow solid (0.5 g, 20%).

Compound 8. Triethylenetetramine (tren) (22 g, 151 mmol) in ethanol (200 ml) was added to a solution of 2-hydroxy-3-(dihexylaminomethyl)-5-nonylbenzaldehyde (200 g, 450 mmol) in dichloromethane (400 ml). The resultant orange solution was stirred at room temperature for 72 h then concentrated and dried *in vacuo* to give an orange oil (192 g, 89%) (Found C, 76.9; H, 11.6; N, 6.9. Calc. for $C_{93}H_{165}N_7O_3$: C, 78.1; H, 11.6; N, 6.9%). MS (FAB, 3-noba) m/z, 1429 (MH$^+$ 74%), which was used without further purification.

Compound 9. 2-Hydroxy-3-(piperidin-1-ylmethyl)-5-*tert*-butylbenzaldehyde (0.6 g, 2.0 mmol) in diethyl ether (25 ml) was added to a solution of tame·3HCl (0.15 g, 0.7 mmol) (tame = 1,1,1-tris(aminomethyl)ethane) and NaOH (0.2 g, 5 mmol) in water (10 ml) and the dark orange mixture stirred for 24 h. The organic phase was separated and dried *in vacuo* to give a yellow solid (0.58 g, 98%), which was used without further purification for the preparation of complexes. MS (FAB, 3-noba) m/z, 889 (MH$^+$ 57%).

Compound 10. 2-Hydroxy-3-(piperidin-1-ylmethyl)-5-*tert*-butylbenzaldehyde (2.0 g, 7.3 mmol) in diethyl ether (25 ml) was added to a solution of tach·3HBr (0.9 g, 2.4 mmol) in NaOH (0.5 g, 12.5 mmol) in water (10 ml) and the mixture stirred for 72 h. The organic phase was separated and dried *in vacuo* to give a yellow solid (1.7 g, 78%) (Found C, 75.6; H, 9.1; N, 9.1. Calc. for $C_{57}H_{84}N_6O_3$: C, 76.0; H, 9.4; N, 9.3%). MS (FAB, thio) m/z, 902 (MH$^+$ 30%), which was used without further purification for the preparation of complexes.

Complexes for X-ray diffraction

[Ni(9)SO₄]·5H₂O. A solution of **9** (0.1 g, 0.1 mmol) in methanol (40 ml) was added to NiSO₄·6H₂O (0.03 g, 0.1 mmol) in methanol (20 ml) to give a green/brown solution which was stirred at room temperature for 78 h. Solvent was removed *in vacuo* to give a brown solid which was washed with diethyl ether/pentane and collected by filtration (0.09 g, 86%) (Found C, 57.3; H, 8.0; N, 7.6. Calc. for $C_{56}H_{94}N_6NiO_{12}S$: C, 59.3; H, 8.3; N, 7.4%). MS (FAB, 3-noba) m/z, 1044 (MH$^+$ 15%). Crystals of [Ni(**9**)SO₄]·5.25H₂O suitable for X-ray diffraction were obtained by slow diffusion of hexane into a dichloromethane solution.

[Ni(9)Cl]Cl. A solution of **9** (0.1 g, 0.1 mmol) in methanol (10 ml) was added to NiCl₂·6H₂O (0.03 g, 0.1 mmol) in methanol (20 ml). The resultant yellow/brown solution was heated under reflux for 2 h, cooled and the solvent removed *in vacuo* to give a brown powder (0.09 g, 88%). Crystals of [Ni(**9**)Cl]Cl·2.5CH₂Cl₂ suitable for X-ray diffraction were obtained by slow diffusion of hexane into a dichloromethane solution.

Solvent extraction studies

Loading isotherms. An aqueous feed with composition similar to that in the Bulong circuit [43] was prepared by dissolving CoSO₄·7H₂O 49.3 mg, NiSO₄·6H₂O 26.3 g, CaSO₄·2H₂O 4.2 g, MgSO₄ 138.4 g, MnSO₄·4H₂O 9.8 mg, ZnSO₄·7H₂O 1.6 mg, and NaCl 170.9 g in distilled water (2 L) and adjusting to pH 4 using NaOH. A 0.1 M solution of **8** in Orform SX7 containing 10 vol% n-decyl alcohol was intimately mixed with the mock Bulong feed solution in the ratios 4 : 1, 2 : 1, 1 : 1, 1 : 2, 1 : 3, 1 :

4, 1 : 6 and 1 : 10 at room temperature for 24 h. Extraction experiments were performed on a minimum of a 20 ml scale (*i.e.* for a 1 : 1 contact 10 ml of organic and 10 ml of aqueous was used). The organic and aqueous phases were separated and both analysed for nickel and sulfur content by ICP-AES.

Acid stripping isotherm. A Ni-loaded organic solution of **8** in Orform SX7 containing 10 vol% n-decyl alcohol was generated by 2 contacts with the mock Bulong feed solution and analysed for nickel (4.5 g L^{-1}). This loaded Orform SX7 solution was intimately mixed with 20 g L^{-1}, 35 g L^{-1} or 70 g L^{-1} sulfuric acid solutions in the ratios 10 : 1, 5 : 1, 2 : 1 and 1 : 1 at room temperature for 1 h. The organic and aqueous phases were separated and both analysed for nickel content by ICP-AES.

Collection and reduction of X-ray data

Data for **6** were collected on a Stöe Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems low temperature device using graphite monochromated Cu-K$_a$ sealed tube X-ray radiation. An absorption correction was applied using the method of Blessing [44] with the program SADABS. [45] Data for [Ni(**9**)SO₄]·5.25H₂O and [Ni(**9**)Cl]Cl·2.5CH₂Cl₂ were collected on a Bruker SMART APEX CCD equipped with an Oxford Cryosystems low temperature device using graphite monochromated Mo-K$_a$ sealed tube X-ray radiation. An absorption correction was applied using a semi-empirical method based on azimuthal measurements [46] for [Ni(**9**)SO₄]·5.25H₂O, whilst for [Ni(**9**)Cl]Cl·2.5CH₂Cl₂ the method of Blessing [44] was used with the program SADABS. [45]

The structures of **6** and [Ni(**9**)SO₄]·5.25H₂O were solved using direct methods and the Patterson method respectively and were refined against F^2 using the program SHELXTL. [47] For **6** a Flack parameter [48] and an extinction parameter were refined. All H-atom positions were calculated and refined as riding or rotating groups. All fully-occupied non-H-atoms were refined anisotropically. The space group for **6** was tested using the symmetry search programs [49] within PLATON. [50] Although the majority of atoms match the symmetry of $P2_1/c$, one of the arms did not and the structure refined better in the lower symmetry space group Pc. One *tert*-butyl group (C41A to C44A) in [Ni(**9**)SO₄]·5.25H₂O is rotationally disordered over two positions in a 25 : 75 ratio and the sulfate is disordered over two positions in a 36 : 64 ratio. Three water molecules (O1W, O2W and O3W, one, O1W, on an inversion centre) were refined as half-occupied. All partially occupied atoms, excluding the sulfate, were refined isotropically. No water H-atoms were found on difference maps or inserted in calculated sites in refinement.

[Ni(**9**)Cl]Cl·2.5CH₂Cl₂ was solved using the Patterson method with the program Dirdif [51] and refined against F^2 as described above. One *tert*-butyl group (C41D to C44D) is rotationally disordered over two positions in a 85 : 15 ratio. The thermal parameters of the major component of the disorder were refined anisotropically whilst C42G to C44G, the minor component of the disorder, were refined isotropically. Disordered solvent regions were treated in the manner described by van der Sluis and Spek, [52] as 445 e per cell, approximating to 2.5CH₂Cl₂ (= 105 e) per formula unit. Details of data collection and structure determination are given in Table 1.

CCDC reference numbers 200690–200692.

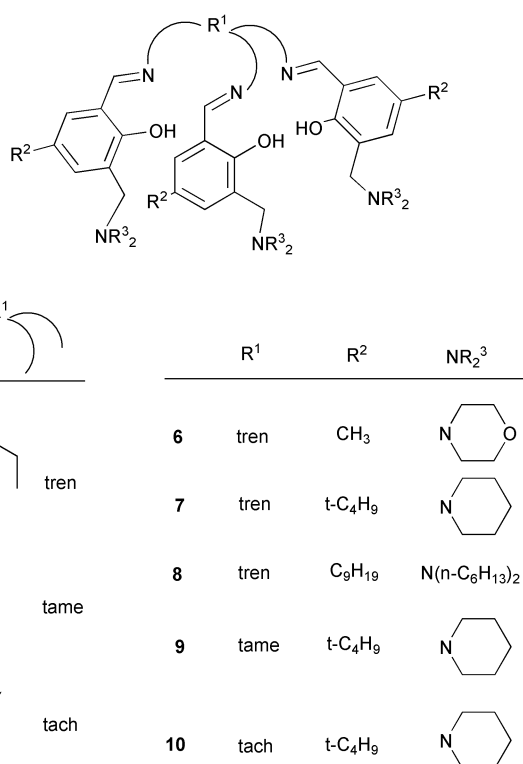See http://www.rsc.org/suppdata/dt/b3/b300176h/ for crystallographic data in CIF or other electronic format.

Results and discussion

Synthesis of ligands and complexes

Whilst the bifurcated "salen-like" ligands in Scheme 1 have been shown [37] to form neutral low spin [NiLSO₄] complexes, the

Table 1 Crystallographic data

Parameter	6	[Ni(9)SO$_4$]·5.25H$_2$O	[Ni(9)Cl]Cl·2.5CH$_2$Cl$_2$
Empirical formula	C$_{45}$H$_{63}$N$_7$O$_6$	C$_{56}$H$_{94.5}$N$_6$NiO$_{12.25}$S	C$_{58.50}$H$_{89}$Cl$_7$N$_6$NiO$_3$
M	798.02	1138.65	1231.22
Crystallographic system	Monoclinic	Monoclinic	Triclinic
Space group	Pc	$P 2_1/n$	$P\bar{1}$
a/Å	22.870 (5)	13.4209 (15)	15.5235(13)
b/Å	18.410 (4)	20.963 (2)	16.4482(15)
c/Å	10.360 (2)	23.789 (3)	28.230(3)
α/°	90	90	96.448(2)
β/°	93.26 (3)	103.006 (2)	105.731(2)
γ/°	90	90	108.900(2)
V/[Å^3]	4354.9 (15)	6521.2 (12)	6403.7(10)
Z	4	4	4
ρ_{calcd}/g cm^{-3}	1.217	1.160	1.277
μ/mm^{-1}	0.654	0.388	0.641
T/K	150(2)	150(2)	150(2)
Unique data (R_{int})	7782 (0.0000)	8533 (0.1433)	21930 (0.0545)
Unique data with $F_o>4\sigma(F_o)$	7161	4019	11688
R_1, wR_2	0.0434, 0.1216	0.1051, 0.2791	0.0678, 0.1711

	R^1	R^2	NR$_2^3$
6	tren	CH$_3$	morpholine
7	tren	t-C$_4$H$_9$	piperidine
8	tren	C$_9$H$_{19}$	N(n-C$_6$H$_{13}$)$_2$
9	tame	t-C$_4$H$_9$	piperidine
10	tach	t-C$_4$H$_9$	piperidine

Fig. 6 Trifurcated ligands providing tricationic sulfate-binding and trianionic six-coordinate metal-binding sites.

slow complexation/decomplexation rates in 2-phase systems‖ and the poor organic phase loading levels do not make them good candidates for development.[53] The trifurcated analogues 6–10 shown in Fig. 6 were selected for study on the grounds that they are likely to be stronger ligands for metal(II) sulfates. A zwitterionic form of the ligands 6–10 has a trianionic N$_3$O$_3^{3-}$ Ni-binding site and a tricationic trisalkylammonium sulfate-binding site and will give an overall neutral NiSO$_4$-complex which is needed to achieve high solubility in non-polar water-immiscible solvents. It is also likely to bind both Ni^{2+} and SO$_4^{2-}$ more strongly than the bifurcated systems as a result of the higher charges on the complexing sites. It was also hoped that formation and decomposition of Ni(II) complexes in the solvent extraction process would proceed more rapidly than the low spin complexes in Scheme 1.

‖ The kinetics of loading and stripping are very poor (>24 hours is needed to approach equilibrium).

The hexadentate ligands 6, 7, 9 and 10 with methyl or *tert*-butyl substituents were isolated as solids with acceptable purity for the preparation of metal salt complexes by adaptation of the methods described previously.[37,39] The more hydrocarbon soluble ligand 8 with mixed isomer/multi-branched nonyl substituents was required in large quantities (>500 g) for solvent extraction experiments and proved more difficult to obtain in high purity. The precursor 2-hydroxy-3-(dihexylaminomethyl)-5-nonylbenzaldehyde was obtained in a substantially pure form by chromatography on a large scale and 8 was obtained in *ca.* 90% purity from the Shiff base condensation with tren. Purification of a 0.1 M solution in 9 : 1 SX7 : decyl alcohol was effected by transferring water soluble Ni-complexing impurities into water, taking the ligand solution through a full load/strip cycle. The solution of 8 was loaded using a 1 M NiSO$_4$ solution, then stripped in 2 stages using concentrated ammonia, to give a residual Ni concentration of 0.5 g L^{-1}. After washing with water this partially loaded solution was used to generate isotherms. The ligands 6–10 show NMR, IR and mass spectra comparable to those of their bifurcated analogues reported earlier.[37,39] The structure of 6 was confirmed by X-ray crystallography.

Complexes of 6, 7, 9 and 10 were formed almost immediately upon mixing alcoholic solutions of the ligand and nickel(II) sulfate. Elemental analysis and FAB mass spectrometry are consistent with the formation of simple 1 : 1 : 1 metal : ligand : sulfate assemblies which exhibit characteristic absorbancies for the sulfate ion in their IR spectra. The formulation as complexes of the trianionic/tricationic ligand zwitterions is confirmed by X-ray structure determinations of [Ni(9)SO$_4$]·5.25H$_2$O and [Ni(9)Cl]Cl·2.5CH$_2$Cl$_2$.

Extraction results

The aqueous mixed metal salt solution used in the loading isotherm experiments [Co 5.3 mg L^{-1}, Ni 2.8 g L^{-1}, Ca 0.5 g L^{-1}, Mg 14 g L^{-1}, Mn 0.4 mg L^{-1}, Zn <0.2 mg L^{-1}, S (as SO$_4^{2-}$) 22 g L^{-1} and Cl (as Cl$^-$) 65 g L^{-1}] has a composition similar to that in the proposed Ni-recovery circuit in Bulong Australia, after cobalt removal using Cyanex 272.[43] This has an unusually high chloride content which arises from the saline bore water used in the leaching process.

Loading isotherms obtained using a 0.1 M solution of unpurified 8 in Orform SX7/decyl alcohol gave a maximum Ni-loading of only *ca.* 4.2 g L^{-1}, representing 71% of the theory. Ni-transfer to the organic phase was particularly poor when high organic : aqueous ratios (>2) were used and was accompanied by a colour change in the aqueous phase from

green to blue. This suggested that impurities in the extractant form stable water-soluble Ni–amine complexes. These impurities were readily removed by putting the extractant through a load/strip cycle (see Experimental section), and the loading isotherm for the purified extractant (Fig. 7) shows a maximum loading of 5.3 g L^{-1} Ni, close to 100% of theory.
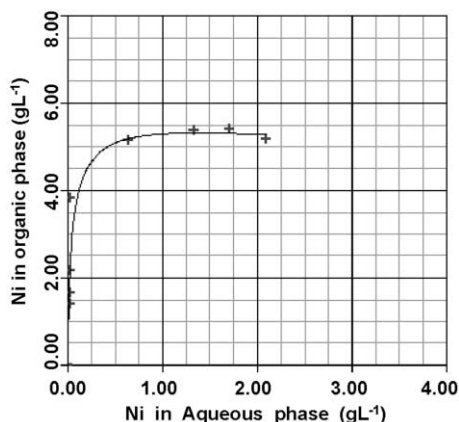

Fig. 7 The Ni-extraction isotherm for purified **8** (0. 09 M in SX7 + 10 vol% n-decyl alcohol) on contact with mock Bulong aqueous feed.[43]

The steepness of the loading isotherm and the associated efficient nickel extraction is consistent with the "subtractive" nature of the process, contrasting with ion exchange solvent extractants. In particular it compares favourably with the isotherms for pH-swing extractants where metal recovery from weakly acid feed solutions is associated with the release of proton to the aqueous phase, lowering pH and depressing the isotherm.

The extractant **8** shows high selectivity for Ni over the other metals in the mock Bulong feed. Ca, Mg, Mn and Zn levels were below detection limits in the organic phase after two 1 : 1 contacts. Whilst the Co-loading is also low (<2 mg L^{-1}) and close to the detection limit, *any* transfer to the organic phase is potentially a problem for the long term operation of a circuit because oxidation to Co(III) will generate complexes which will be very difficult to strip and could lead to a steady build up of Co in the organic phase, effectively poisoning the extractant.

Stripping with sulfuric acid could provide a potential route for recycling the extractant and generating an electrolyte for Ni-production (Fig. 8).
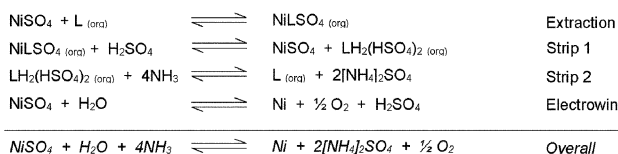

Fig. 8 Recovery of Ni from a sulfate stream using a $NiSO_4$ extractant such as **8** followed by acid stripping and reagent neutralisation.

Solutions with a range of compositions typical of spent electrolyte from Ni-electrowinning (see Experimental section) gave almost quantitative removal of nickel, as illustrated by the isotherm shown in Fig. 9.

These isotherms and the assumption that the reagent **8** could be effectively regenerated in its neutral form and recycled, for example as in Fig. 8, allow the nickel recovery to be modelled using the MINCHEM software.[54] A 98% recovery is predicted (Fig. 10) for a circuit with two extraction stages and one stripping stage. This will generate an electrolyte with 55 g L^{-1} Ni, the concentration currently proposed for the Bulong circuit.[43]
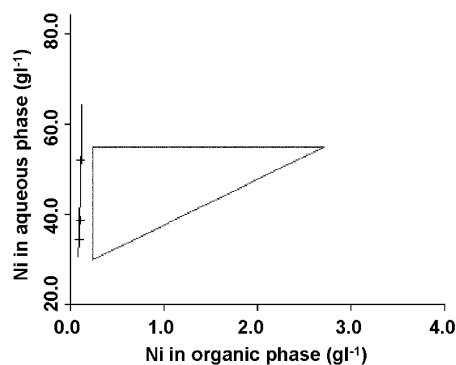

Fig. 9 The stripping isotherm for Ni-loaded **8** (0.09 M in SX7 + 10 vol% n-decyl alcohol after equilibration with excess mock Bulong aqueous feed[43]) with H_2SO_4 (35 g L^{-1}) containing $NiSO_4$ (30 g L^{-1}). Also illustrated is the McCabe–Thiele construction (triangle) assuming a stage efficiency of 90% and an aqueous : organic phase ratio of 1 : 1, demonstrating that efficient Ni-stripping is achievable in a single stage.
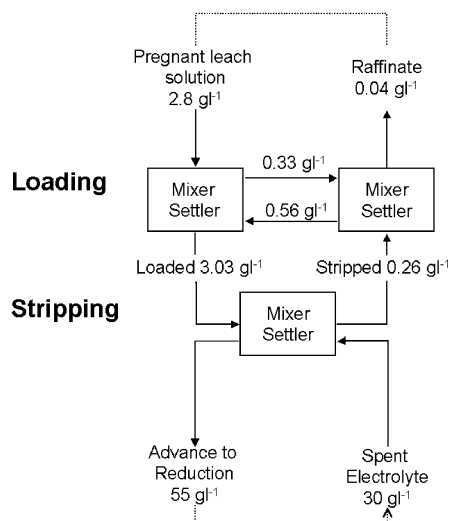

Fig. 10 A circuit and the predicted Ni-concentrations of streams to achieve >98% recovery of $NiSO_4$ and generate a 55 g L^{-1} Ni electrolyte for Ni recovery from a mock Bulong feed using **8** (0.1 M in Orform SX7 with 10% n-decyl alcohol). In the MINCHEM software[54] 1 : 1 organic to aqueous ratio and a 90% approach to equilibrium in mixer settlers was assumed.

On paper the simplicity of this circuit compares very favourably with the one currently proposed for the Bulong operation which uses the pH-swing extractant versatic acid,[43] with 4 extract and 3 strip stages plus extractant recovery steps (versatic acid has an appreciable solubility in aqueous media). However, based on other observations of the properties of the prototype extractant **8**, two major problems arise. The extractant was found to show a high selectivity for $NiCl_2$ over $NiSO_4$ when contacted with a mixed chloride/sulfate feed of the Bulong type. The loaded organic solutions had undetectable levels of sulfate as judged by sulfur analysis by ICP OES, whilst chloride levels, determined by titration with $AgNO_3$ after dissolution of samples in thf/sodium hydroxide solution, corresponded closely to a 2 : 1 molar ratio with Ni loadings (by ICP OES). More seriously, in these preliminary tests stripping with sulfuric acid was accompanied by ligand hydrolysis, leading to very significant reductions in Ni-loadings when it was taken through further cycles of extraction. The sensitivity of **8** to hydrolysis was unexpected as the 5-nonyl-derivatives of salicylaldoximes show long lifetimes when used in kerosene as Cu-extractants.[7]

A number of approaches to dealing with the $NiCl_2$-loading from the Bulong feed can be considered. (i) The very high selectivity for extraction of chloride over sulfate may justify the

development of a circuit for electrowinning from chloride solution, ** all components of which have been established previously. (ii) The loaded organic could be stripped with ammonia to generate [Ni(NH₃)₆]Cl₂, a potential feedstock similar to that which has been used for the Sherrit hydrogen reduction process.[55,56] An advantage of this approach is that it avoids stripping under acidic conditions which have so far resulted in extensive hydrolytic degradation of **8**.

Contacting a fully NiCl₂-loaded solution of **8** with concentrated aqueous ammonia solutions leads to efficient stripping and regeneration of the neutral extractant, but phase disengagement has been poor in the experiments performed to date due to the low solubility of [Ni(NH₃)₆]Cl₂ which results in formation of a third phase and we have been unable to generate a full strip isotherm.

The high Cl⁻/SO₄²⁻ selectivity shown by **8** is consistent with the Hofmeister series.[57,58] Attempts to reverse this order require an understanding of the anion binding modes in the trifurcated ligands **6–10**.
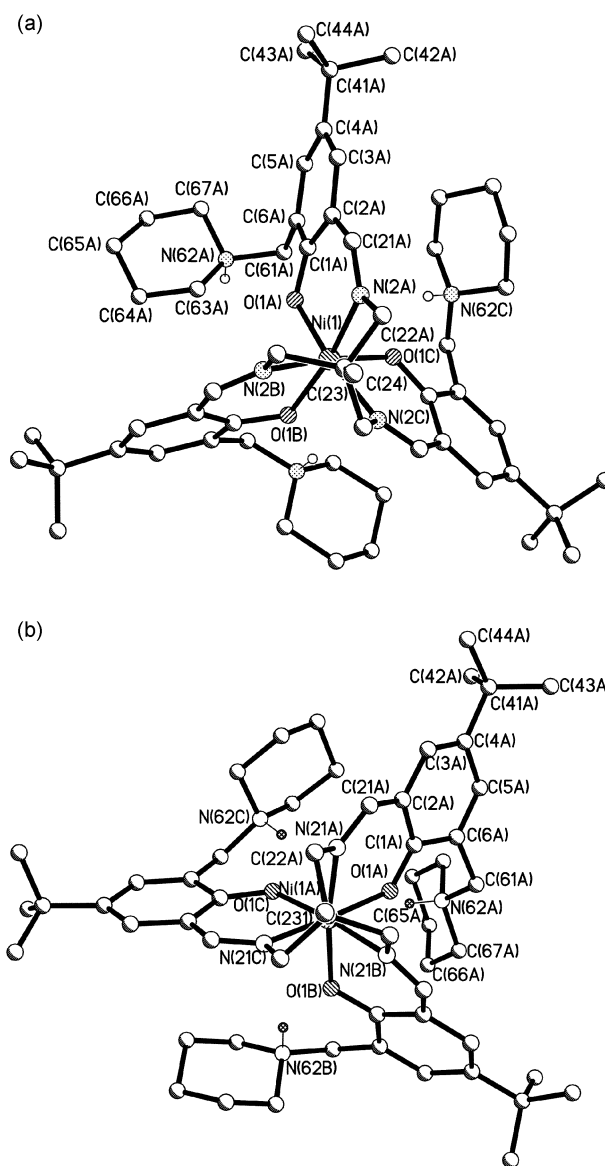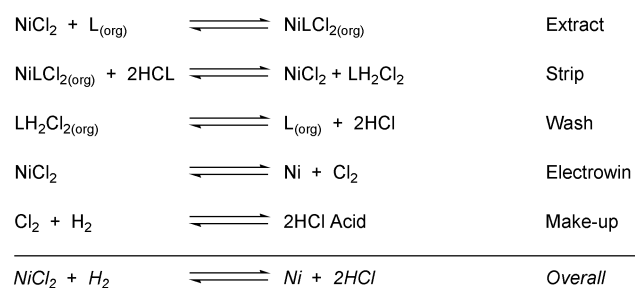
X-Ray structure determinations

Incorporation of Ni^{2+} into the $N_3O_3^{3-}$ donor set will influence the disposition of the pendant teriary amine groups, and hence the efficacy of anion binding. The free ligand **6** has a very extended structure in the solid state (Fig. 11), with the tertiary amine groups more than 5.2 Å from their centroid.
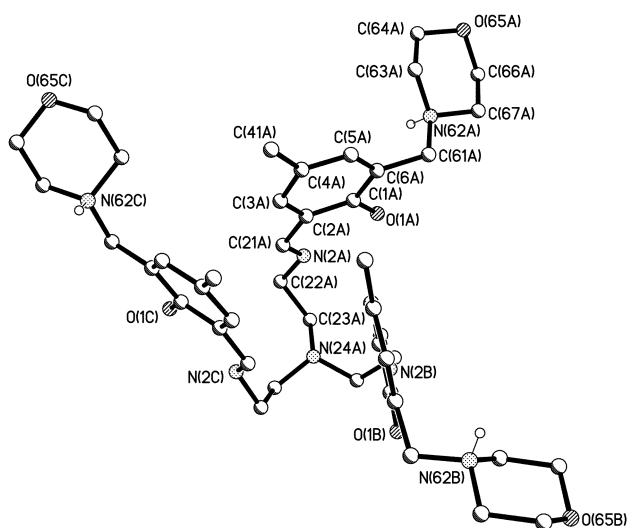
Fig. 11 The structure of the free ligand **6** showing one of the two crystallographically independent molecules. The other was assigned similar atom labels for its three arms D, E and F. The tertiary amine N-atoms N62A,B,C and N62D,E,F are located 5.393(5), 6.823(5), and 6.553(5) and 5.231(5), 6.349(5) and 6.156(5) Å from their centroids respectively in the two molecules.

Formation of the NiSO₄ and NiCl₂ complexes of **9** results in a "3-fold propeller" arrangement of the salicylaldiminato arms

** An excellent materials balance results from the sequence

NiCl₂ + L₍org₎	⇌	NiLCl₂₍org₎	Extract
NiLCl₂₍org₎ + 2HCL	⇌	NiCl₂ + LH₂Cl₂	Strip
LH₂Cl₂₍org₎	⇌	L₍org₎ + 2HCl	Wash
NiCl₂	⇌	Ni + Cl₂	Electrowin
Cl₂ + H₂	⇌	2HCl Acid	Make-up
NiCl₂ + H₂	⇌	*Ni + 2HCl*	*Overall*

Fig. 12 The [Ni(**9**)]²⁺ units in (a) [Ni(**9**)SO₄] and (b) [Ni(**9**)Cl]Cl viewed down the pseudo-3-fold axes defined by the CH₃–C bond of the capping tame unit. The anions and all H-atoms apart from the trialkylammonium protons have been omitted for clarity.

of the ligand (Fig. 12) and a pseudo-octahedral coordination geometry (Table 2).

Incorporation of the Ni^{2+} into the metal binding site has constrained the tertiary amine atoms N62A *etc.* to lie much closer to the ligand's pseudo-3-fold axis (< 3.7 Å) and from their centroids (Table 2).

The presence of water in the lattice of the [Ni(**9**)SO₄] structure is associated with complex hydrogen-bonding patterns and consequently does not help us to predict the mode of binding of sulfate in non-polar, water immiscible media. The interpretation is further complicated by disorder of the sulfate group. One of the piperidinium protons (H62A) forms a bifurcated H-bond to two oxygen atoms on the higher occupancy sulfate ion (Fig. 13). In this hydrated structure, in contrast to the structures of the low spin NiSO₄ complexes,[37] two of the piperidinium protons H62B and H62C make close contacts to the phenolate oxygen atoms, O1B and O1C, in the same arms of the ligand (Fig. 13). In the NiCl₂ complex in both crystallographically independent molecules all the piperidine nitrogen atoms make fairly close contacts (2.57 to 3.15 Å) to their neighbouring phenolate oxygen atoms. One of the chloride ions lies close to the pseudo-3-fold axis and is bonded strongly to one piperidinium group and weakly to another (N62A and N62C in

Table 2 Bond lengths (Å) and angles (°) in the Ni-coordination spheres of [Ni(**9**)Cl]⁺ and [Ni(**9**)SO₄] [a]

	[Ni(**9**)Cl]⁺						[Ni(**9**)SO₄]		
	part A [b]	part B	part C	part D	part E	part F	part A	Part B	part C
Ni(1)–N(2)	2.052(4)	2.056(4)	2.035(3)	2.043(4)	2.033(4)	2.053(4)	2.059(8)	2.081(7)	2.069(8)
Ni(1)–O(1)	2.029(3)	2.045(3)	2.053(3)	2.025(3)	2.059(3)	2.059(3)	2.010(6)	2.044(6)	2.039(6)
O(1)–Ni(1)–N(2)	89.23(12)	87.44(13)	89.78(12)	90.21(13)	89.85(13)	87.10(14)	89.0(3)	87.5(3)	87.1(3)
'O1–Ni(1)–O1'	87.24(11)			90.18(12)			87.0(3)		
'O1–Ni(1)–O1''	91.08(11)			87.37(12)			85.7(2)		
O1'–Ni(1)–O1''		86.92(11)			88.84(11)			90.7(3)	
'N2–Ni(1)–N2'	85.00(15			86.99(15)			85.2(3)		
'N2–Ni(1)–N2''	87.64(13)			84.97(16)			88.9(3)		
N2'–Ni(1)–N2''		89.74(13)			90.21(15)			87.4(3)	
[d]N(62)···centroid	3.108(5)	3.584(5)	3.244(5)	3.069(5)	3.352(5)	3.715(5)	3.323(12)	3.362(12)	3.447(12)

[a] Values compare well with Ni(II) complexes of hexadentate ligands with N₃O₃³⁻ donor sets.[60–62] [b] Parts A, B, and C refer to chemically equivalent arms of the ligand. For [Ni(**9**)Cl]⁺, parts D, E and F refer to a second crystallographically independent complex in the asymmetric unit. See Fig. 12 for the definition of atom labels. [c] The single prime and double prime refer to chemically equivalent atoms in parts B and C or E and F respectively. [d] The e.s.d.s are estimated as the mean of the e.s.d.s for the N62 ··· N62', N62 ··· N62'' and N62' ··· N62'' contacts.
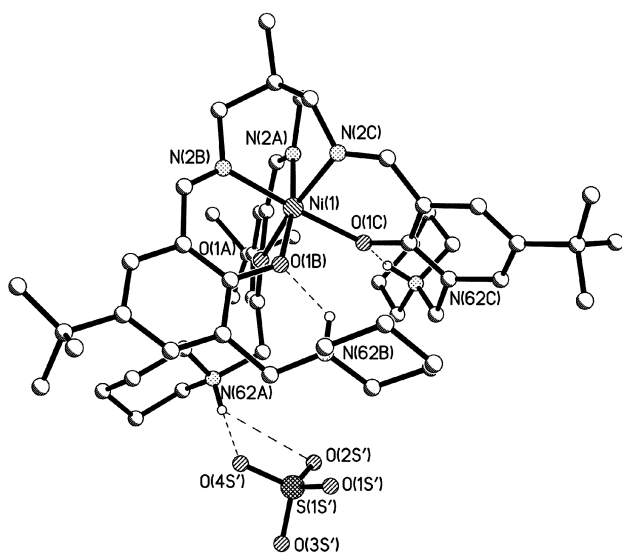
Fig. 13 Intramolecular H-bonds from the piperidinium groups in the hydrated [Ni(**9**)SO₄] complex; N62 contacts to phenolate oxygen atoms O1B and O1C are 2.64(1) and 2.67(1) Å respectively and to the two sulfate oxygen atoms 2.659(2) and 2.755(4) Å.

the complex shown Fig. 12). The other chloride ion is *exo* hydrogen bonded, crosslinking complex units. It is probable that coordination of the chloride ions in hydrocarbon solutions of **8** involves a substantially different arrangement of electrostatic and H-bonding to the di-n-hexyl substituted ammonium groups, to account for the high strength of this reagent as a NiCl₂-extractant.

It is also likely that the sulfate ion interacts with the pendant ammonium groups in **8** in a different manner in hydrocarbon solutions. In the structure of [Ni(**9**)SO₄] (Fig. 13) rotation about the C6–C61 and C61–N62 bonds would re-align the piperidinium proton towards the pseudo-3-fold axis of the molecules and thus allow further H-bonds to be formed to a sulfate dianion lying close to this axis. Preliminary calculations indicate that relatively small energy differences are involved in these bond rotations.[59]

Conclusions

The hexadentate trifurcated ligands **6–10** readily form complexes with NiCl₂ and NiSO₄, and are better extractants of Ni(II) salts than their bifurcated, "salen-like", analogues, both on kinetic and thermodynamic grounds. They show potential for commercial development provided derivatives or formulations are used with *greatly* enhanced stability towards hydrolysis. The very high selectivity for transport of NiCl₂ over

NiSO₄ is unexpected and whilst not considered as part of a strategy to process sulfidic ores *via* oxidative leaching, for which electrowinning from sulfate media was envisaged, may prove to be very useful in chloride-based processes.

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